

THE KINETICS OF OIL SHALE CHAR GASIFICATION

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INTRODUCTION

During oil shale retorting, whether it be by in-situ or surface techniques, a certain fraction of the organic carbon is left behind on the retorted shale. This "char" contains a significant fraction of the available energy in the raw shale and can actually supply all the energy for the retorting process for shales assayed at 20 gallons/ton or greater (1). To recover this energy, the char can be burned in air or gasified in O₂-steam environments; the latter in order to produce a low to medium BTU gas which can be burned elsewhere in the plant. Consequently we have been conducting kinetic studies of the reactions of oil shale char in an on-going research program under the sponsorship of DOE. Earlier we reported on the results of our oxidation experiments (2) and here we will report on our work with CO₂ and steam gasification of the char.

EXPERIMENTAL

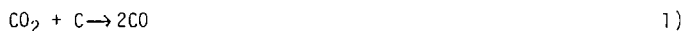
All of the gasification experiments were conducted with the same apparatus employed in the earlier oxidation work and has been described in detail elsewhere (2). As before, powdered shale samples (200 mesh) of previously retorted oil shale from the Parachute Creek member in Colorado were suspended from an electrobalance and placed in a furnace. In this way continuous gravimetric readings were available to monitor the consumption of the char. The off-gases were analyzed on a Carle gas chromatograph equipped with a Carbosieve B column. The retorted raw shale assayed at 50 GPT and was exposed to CO₂ pressures as high as 100 KPa and H₂O pressures as high as 75 KPa. Because there was evidence of the water gas shift reaction during steam gasification, separate experiments were also conducted in order to determine the rate of this reaction as a function of temperature and concentration of the reactant gases.

Since the char reactions can be accompanied by mineral decomposition reactions, every attempt was made to isolate the pertinent reactions. When studying CO₂ gasification the shale was first raised to 900 K in a helium environment in order to allow irreversible dolomite decomposition to take place. The predetermined CO₂-He mix was then fed to the reactor and the temperature was raised to the desired value. Since steam gasification takes place at elevated temperatures (>975K) it was necessary to first decompose the calcite present in the shale to CaO. If this was not done, then calcite decomposition would have occurred simultaneously with steam gasification. This was accomplished in a helium environment at 950K, a temperature high enough for calcite decomposition but low enough to minimize char consumption via CO₂ gasification. A few experiments were also conducted on acid leached shale. Here the shale was first soaked in either HCl or H₂SO₄ which removed Ca, Fe and Mg in the former case or converted these elements to their sulfates in the latter. Studies of the water gas shift reaction were conducted after reacting the calcite with the silica present in the shale to form inert silicates. For these experiments the shale was first decharred in 10% O₂ at 700K and then heated to 1150K in one atmosphere of CO₂ for 12 hours. The presence of CO₂ prevented decomposition of calcite to CaO during this procedure. The shale was then cooled to the desired temperature and various CO/H₂O/CO₂/H₂ mixtures were admitted to the reactor.

RESULTS

CO₂ Gasification. The rate expression given in Equation 2) was found to give a good correlation of the data, where r_{cc} is the CO₂-char reaction rate in moles/min.,

C is the unconverted char in moles, the partial pressures are in kilopascals and the activation energy is in kcal/mole. Although there was indisputable evidence of the



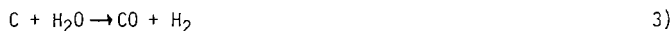
$$\frac{r_{\text{CC}}}{C} = \frac{k_1 P_{\text{CO}_2}}{1 + K_1 P_{\text{CO}_2} + K_2 P_{\text{CO}}} \quad (2)$$

$$k_1 = 4.7 \times 10^6 \exp [-44.3/RT]$$

$$K_1 = 0.05, K_2 \sim 0.4$$

inhibiting effect of CO, the value of K_2 is, at this time, only an approximation. The form of Equation 1) explains, to some degree, the results obtained by Burnham (3) who reported a reaction order with respect to CO_2 of $0.2 \pm .2$. However, the rates predicted by Equation 1) are about a factor of three less than those measured by Burnham.

Steam Gasification. Steam gasification of the char was found to produce a preponderance of H_2 and CO_2 with only a few percent CO. This is apparently due to significant water gas shift reaction rates so that steam gasification proceeds according to Equations 3) and 4). A separate determination of the rate of Equation 3) was



accomplished by initial rate measurements with the result that

$$\frac{r_{\text{CC}}}{C} = k_2 P_{\text{H}_2\text{O}}^5 \quad (5)$$

$$k_2 = 210 \exp [-20.6/RT]$$

As expected, the spent shale prepared by the procedure described above was found to catalyze the water gas shift reaction and a reaction rate expression is given in Equation 6).

$$r_{\text{wg}} = \frac{k_3 (P_{\text{CO}} P_{\text{H}_2\text{O}} - 1/K_E P_{\text{H}_2} P_{\text{CO}_2})}{1 + K_3 P_{\text{CO}_2} + K_4 P_{\text{H}_2\text{O}}} \quad (6)$$

where $k_3 = 0.25 \exp [-19.6/RT]$

$$K_3 = 0.028, K_4 = 0.05$$

and K_E is the thermodynamic equilibrium constant.

Equation 6) was found to be valid only for $P_{\text{CO}_2} > 10\text{KPa}$. At pressures between zero and 10KPa, the reaction rate *increased* with increasing P_{CO_2} . It is hypothesized that the sweep gas effects partial oxidation/reduction of the iron present in the shale and that iron is catalyzing the shift reaction. To test this, oxidation/reduction experiments of the spent shale were also carried out. The weight changes were found to approximate those expected from the quantity of iron present and the rates appeared to be first order with respect to unreacted iron and reactant gas concentration. At 1040K the rate constants for oxidation in CO_2 and reduction in CO or H_2 were all comparable at about $30 (\text{KPa}\cdot\text{min})^{-1}$.

The steam gasification rates for acid leached shale were found to be as much as a factor of five lower than those measured with thermally decarbonated shale. This is similar to our earlier measurements with char oxidation(1).

Mixed Gasification. A series of experiments were also conducted using various mixtures of CO_2 and H_2O in the sweep gas. The overall reaction rate expressions previously derived at Lawrence Livermore Laboratories (3,4) as well as those given here

were numerically integrated in order to provide a basis of comparison between the two laboratories and to see if isolated kinetic experiments could be used to predict mixed gasification results.

In general the Livermore results predicted char consumption rates which were much higher than those observed for mixed gasification runs with $P_{CO_2} > 10\text{KPa}$. The kinetic results from this work gave reasonable matches to the data at $P_{CO_2} < 15\text{ KPa}$ but also predicted much higher rates at CO_2 pressures greater than 20 KPa. An example of these results is shown in Figure 1 for a 50-50 mix of CO_2 and H_2O at 980K. In this case the dashed curve corresponds to the predictions of both laboratories and the experimental results are shown as data points. The data clearly exhibit a much lower char consumption rate than predicted. Also shown in this figure are the predictions assuming that only CO_2 gasification takes place. Surprisingly the assumption provides a reasonable match to the experimental data and suggests that the presence of CO_2 is somehow inhibiting steam gasification. If, as suggested by our char oxidation studies (1), CaO acts as a steam gasification catalyst, an explanation for these results can be given. That is, the mixed gasification experiments were conducted on shale which had only been subjected to dolomite decomposition. Thus, at the initiation of mixed gasification the calcite was still present in the shale and would not decompose at these temperatures if $P_{CO_2} > 10\text{KPa}$. Since this would prevent formation of CaO , there would be no catalytic activity and steam gasification rates could be anywhere from a factor of 3-10 lower than those measured in the presence of CaO and given by Equation 4).

REFERENCES

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CHAR CONSUMPTION FOR EXPERIMENT T-8 $\text{PCO}_2 = .5 \text{ ATM}$, $\text{PH}_2\text{O} = .5 \text{ ATM}$

$T = 980^\circ\text{K}$

